

Role of Gypsum Wastes in Polluting Groundwater and Enhancing Eutrophication in Coasts of Aqaba

*Mohammad Al-Farajat*¹⁾

¹⁾ Assistant Prof., Institute of Earth Sciences and Environment, Al al-Bayt University, Jordan,
e-mail: alfarajat@aadu.edu.jo

ABSTRACT

This study deals with industrial pollution resulting from residual solid wastes that lead to eutrophication processes in coastal systems in hydro-geological and geochemical contexts. Fertilizers Factory in Aqaba Governorate in Jordan was established in 1982. The factory has been disposing solid industrial wastes of gypsum in an area lying at a distance of some hundred meters to the east of the factory since its establishment. Twenty five million tons of wastes have been accumulated since that time and form presently hills of gypsum.

About 10 % by volume of the produced waste consists of water which was found to be rich in phosphate and nitrates. This water partly percolates into the permeable aquifer composed of alluviums causing pollution, and is discharged into the marine environment as submarine groundwater discharge. The study investigated the nature and geology of the hills of gypsum, mineralogy and geochemistry of gypsum, chemistry of impacted soils water, groundwater and seawater. Knowing that the gypsum hills are located some hundred meters from the coast of the Gulf and that about 2 million cubic metres of water are still entrapped inside them, with the presence of sun rays all around the year in this arid region, submarine groundwater discharge enriched with phosphate and nitrate allowed algae growth and consequently the appearance of the primary features of eutrophication in the coasts.

KEYWORDS: Fertilizers' manufacturing, Industrial pollution, Arid regions, Coastal aquifers, Submarine groundwater discharge, Eutrophication.

INTRODUCTION

Fertilizers Factory of Phosphate Company in Jordan is located about 20 km south of Aqaba city in the industrial complex. The factory overlooks the coast of the Gulf of Aqaba from its eastern part. It utilizes the phosphate rock mined and transported from central Jordan to produce a final phosphate fertilizer product, which contains two elements; N and P. Another end product in this factory is aluminum fluoride resulting from using aluminum hydroxide and fluosilicic acid. The later is a non-

favorable by-product of the reaction between phosphate rock and sulfuric acid (Fig. 1). Through the industrial processes, solid secondary gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is produced, and is considered as solid industrial waste that can't be recycled or reused due to the limited economic resources and its content of impurities. The only solution for the produced huge amounts was to dispose them nearer to the factory where permission for that was obtained in 1980 from Aqaba Regional Authority. The study area locates between E $34^\circ 58' 03''$ - $35^\circ 00' 09''$ and N $29^\circ 21' 27''$ - $29^\circ 22' 39''$.

The environmental authorities in the Aqaba Governorate relate the hills of gypsum only to visual type of pollution.

Accepted for Publication on 15/7/2009.

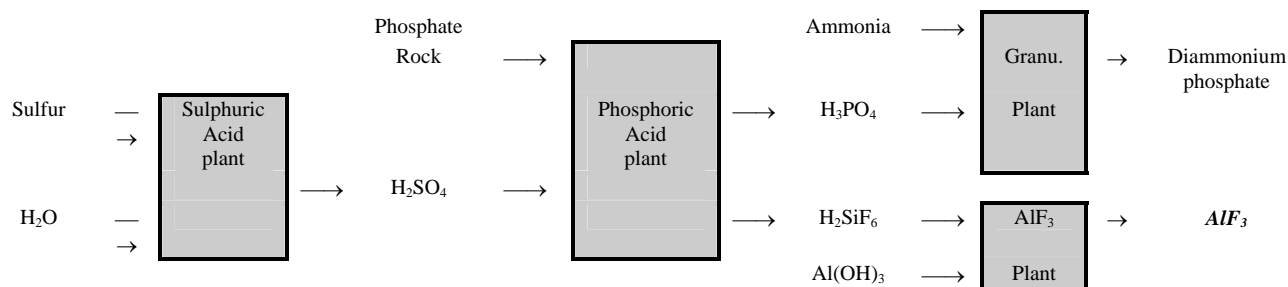


Figure (1): Summary of the manufacturing process of the fertilizers in the factory.

The climate of the area is arid, dry and hot. June, July and August are the hottest months of the year, with average monthly temperatures ranging between 30.6 and 32.1 °C. December, January and February are the winter months, with mean temperatures ranging between 14.9 and 17.6 °C. Rainfall amounts average around 37 mm per year, with actual evaporation of 90% and potential evaporation of around 4000 mm/year (Directory of Meteorology of Jordan, 2007).

Internal reports of the factory (2007) show that more than 20 million tons of gypsum wastes had been deposited in its eastern parts (Figure 2). The reports mention that a sudden huge amount of liquids flooded from one of the waste hills in Nov./2005 and the flood lasted for 3 days. The volume of flood was estimated at more than 50,000 cubic meters.

The sediments underlying the gypsum hills consist of permeable alluvium and permit solutes to infiltrate and percolate vertically into the groundwater body. This may affect the composition of seawater and marine ecology because the groundwater flow is oriented sea-ward (Al-Farajat, 2002).

The disposed amounts of gypsum are growing daily occupying increasing-prices land areas that belong to the city of Aqaba which is a special economic zone since the year 2000. Sudden flash storms and thunder rains in winter may produce floods along the upstream wadis flashing the gypsum into the marine water. Studies on their impacts on soil, marine environment and groundwater have not yet been carried out. Besides the vulnerability of the area to pollution, many tourism and recreation units are built directly to the northern part of the industrial complex. Tourism activity is considered as

one of the most important sources of income and hard currency of Jordan.

The current study aims at evaluating the impacts of the solid gypsum disposal site on the underlying aquifer and on the marine water in the coastal water west of the factory.

Open files of the Marine Science Station of Aqaba (2000) show that the Gulf of Aqaba, the northernmost extension of the Red Sea, is a semi-closed sea 180 kilometer long, oriented north-to-south. It is bounded by four states; Egypt and Saudi Arabia border the west and east, respectively, while Jordan and Israel both have small coastlines at the northern edge of the Gulf. In its physical and biological features, the Gulf of Aqaba is unique in a number of ways. It is a good home to the coral reef ecosystems, due to the exceptional tropical climate of the area. The ecosystem of the gulf is a spectacular one, but is highly vulnerable to rapid environmental changes. More than 300 individual sub-species of coral, a remarkably high number in comparison to other tropical areas, are the key to the Gulf ecosystem. Coral reefs depend on two principal environmental elements: clear water free from sediments and steady, slow currents to carry off waste and provide nutrition. In this regard, the Gulf of Aqaba is exceptionally well-suited for a mature coral reef ecosystem. The deep, still waters of the gulf allow sediment to settle, and the bright sunshine penetrates the water as far as 100 meters. As a result, coral formation – both reef building and soft coral – is extensive and unusually deep in the gulf. The slow, circular currents of the Gulf of Aqaba provide abundant nourishment without endangering coral polyps, and the high levels of dissolved oxygen in the warm waters allow luxuriant coral growth.

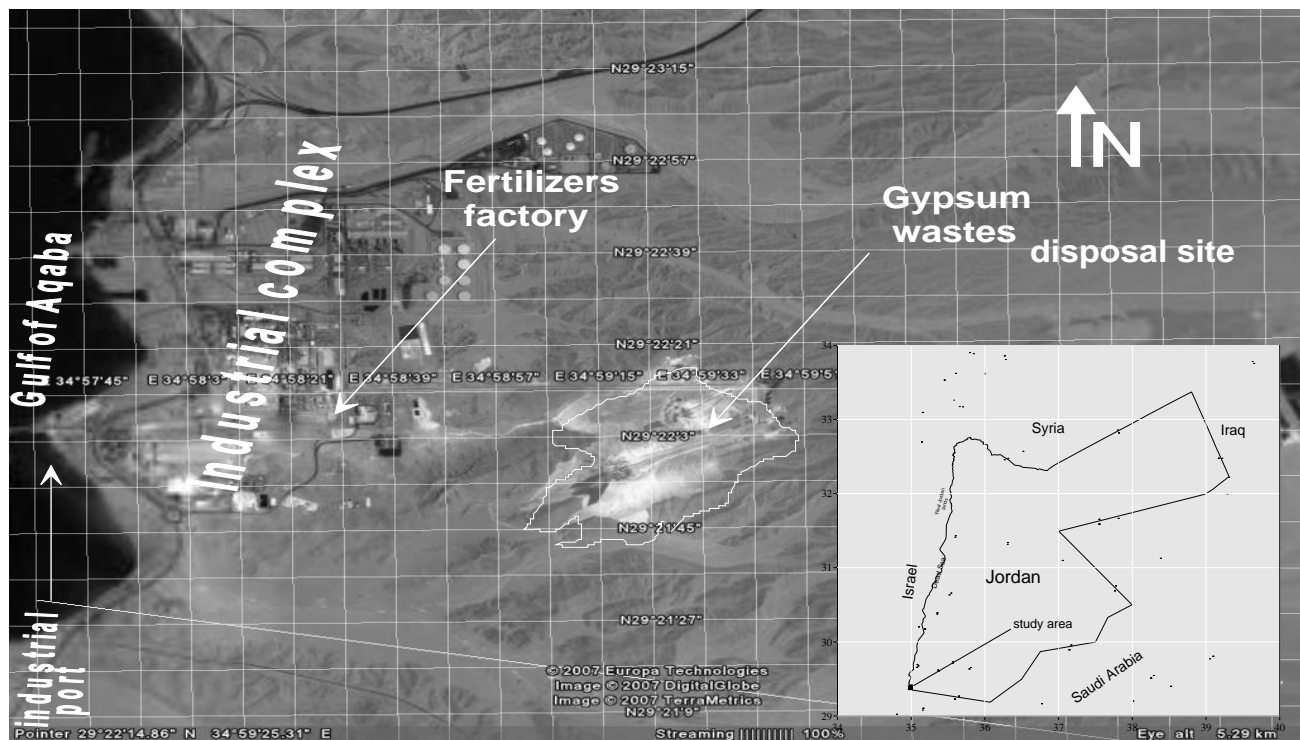


Figure (2): Location of the fertilizers factory and the hills of gypsum, overlooking the Gulf of Aqaba (Source: Google Earth 2007).

The International Oceanographic Commission for the United Nations Educational and Scientific Commission defines marine pollution as: "Introduction by man directly or indirectly of substances into the marine environment resulting in such deleterious effects as harm to living reduction of amenities" (Katayal and Satake, 1996). An increase in the nutrients' content (nitrogen and phosphorus) results in eutrophication processes and becomes enhanced in semi-arid areas by temperature and light illumination, which are the two predominant factors in biological production. Phosphorus is usually the main nutrient responsible for freshwater eutrophication, whereas nitrogen is the primary nutrient causing eutrophication along coastal areas and seas.

Al Farajat (2002), using DRASTIC Index, declared all the coastal zones in the city of Aqaba as highly vulnerable zones for human activities. Al-Ouran (2005) studied the anthropogenic impacts of the Aqaba city on the marine life in terms of the coral reefs. The Science

Marine Station of Aqaba which belongs to the University of Jordan is responsible for monitoring programs of the marine water and aquatic life of the Gulf of Aqaba in the Jordanian water.

METHODOLOGY

For the purpose of this study, a field survey was carried out during which the gypsum hills were studied for their nature, type and topography, and to collect samples. Samples were investigated on their mineralogy and constituents using XRD and XRF techniques. Samples have been chosen from old and modern disposal sites some centimetres below surface to avoid impacts of impurities. Texture and internal structures were studied using Scanning Electron Microscopy (SEM) technique. Gypsum water was obtained from leakage areas in wadis between the hills and investigated regarding its chemistry of major and trace elements and oxides using titration method, ICP and atomic absorption instruments. The

same methods have been applied on the groundwater samples collected from the fertilizers observation well some hundred meters from the disposal site to the west. Seawater samples were collected close to the industrial

port of the industrial complex and analyzed for their contents of NO_3 and PO_4 . The circulating gypsum water was investigated and its impacts on the Gulf's water were identified.

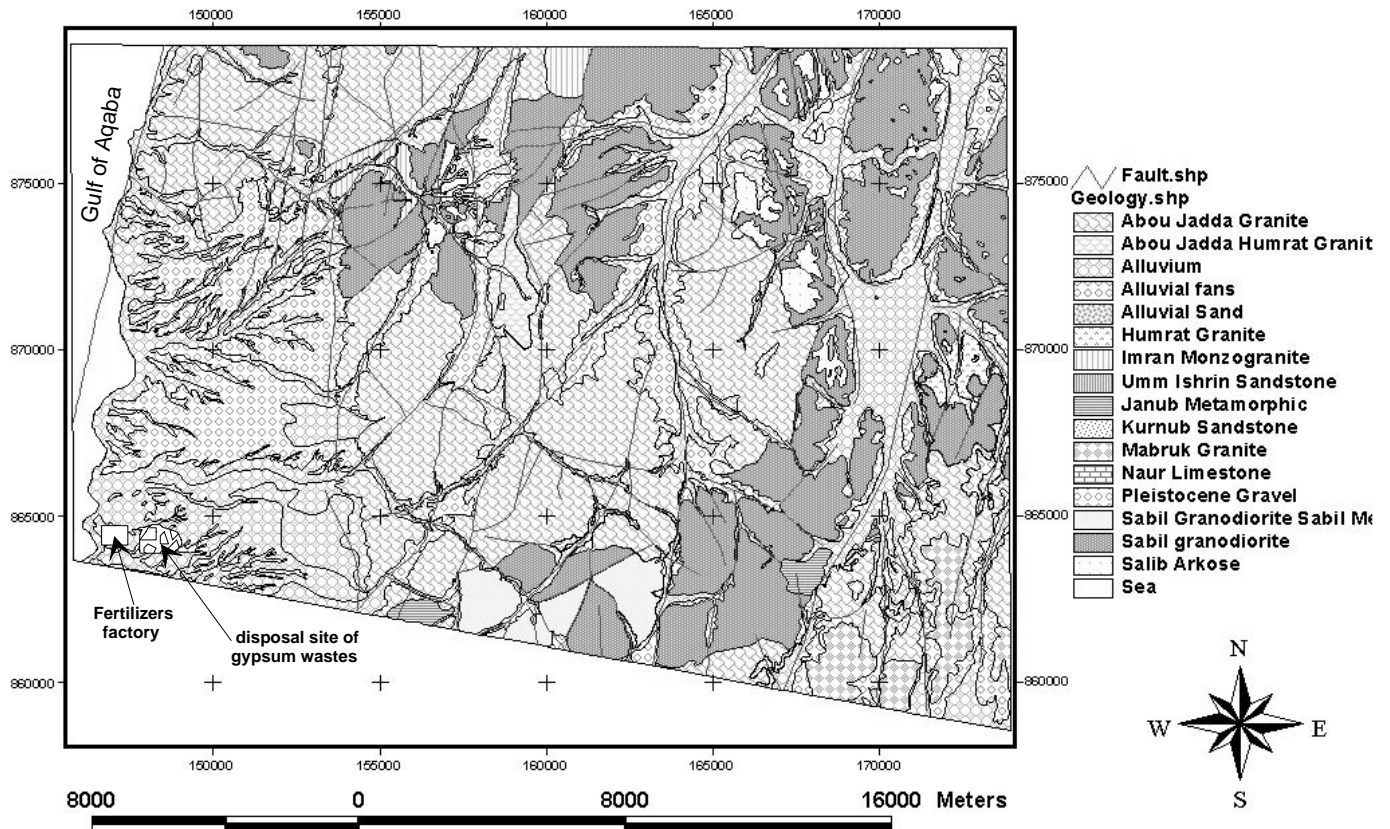


Figure (3): Geological map of the study area (Source: NRA, 2007).

Quality assurance and quality control of the analytical methods have been carried out in the sampling processes of the solid gypsum and water samples, and during the laboratory works regarding all the instruments which have been used. XRD and XRF instruments of the Institute of Earth and Environmental Sciences in Al al-Bayt University in Jordan that have been used in this study are well calibrated using known samples specialized for calibrating purposes. The American Standard Method for Water Analyses and German DI-Norms were used in the analyses of different parameters.

Geological Settings and Study Area

The GIS based geological map of the area (NRA, 2005) shows the different rock units in the area (Fig. 3). The area is a part of the south-north extending transform Dead Sea Fault and forms a basin. The basin is bounded by several faults forming a graben. Alluviums and Pleistocene gravels form thick covers overlying the Pre-Cambrian basement complex (NRA, 1987).

Hydrogeologically, the area where the factory locates consists of a structural basin bounded by faulting systems filled with alluvium forming a type of groundwater aquifers with subsurface barriers. The aquifer is recharged

from infiltration of flood water along the side wadis incised into the eastern granite mountains (Al-Farajat, 2006).

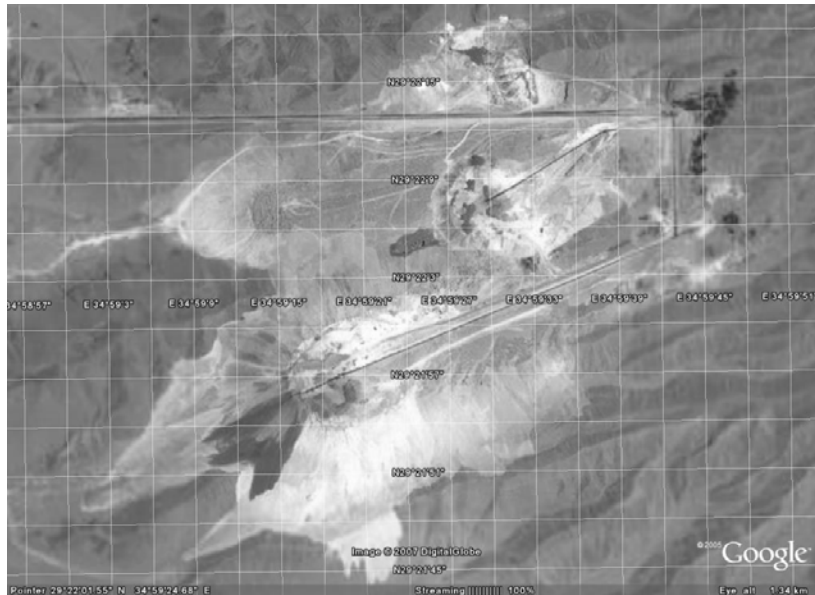


Figure (4): Tones of the color of the gypsum wastes on space photo, white color points to new wastes, while dark gray color points to old disposal sites (Source: Google Earth, 2007).

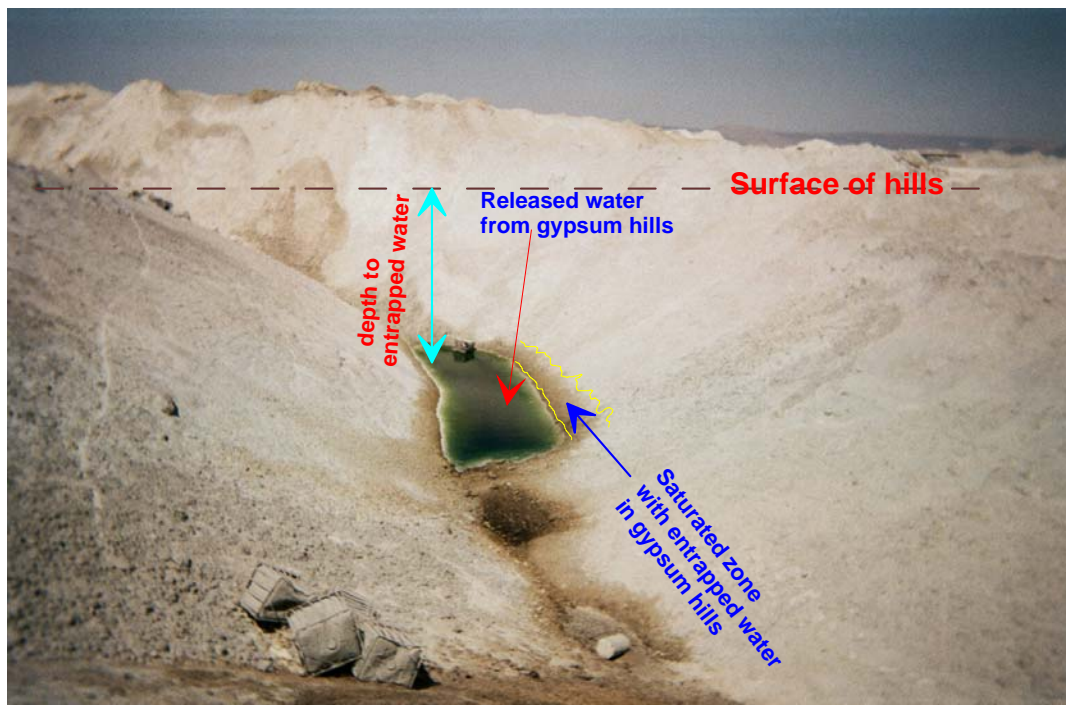


Figure (5): Water leakage from the gypsum wastes collecting between two hills, creating a pool with an area of about 40 m².

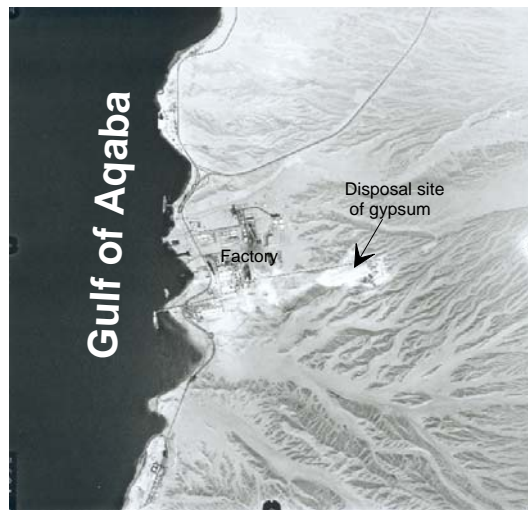


Figure (6): Aerial photo showing wadi systems around the gypsum wastes (in white)
(Source: RGCI, 1998).

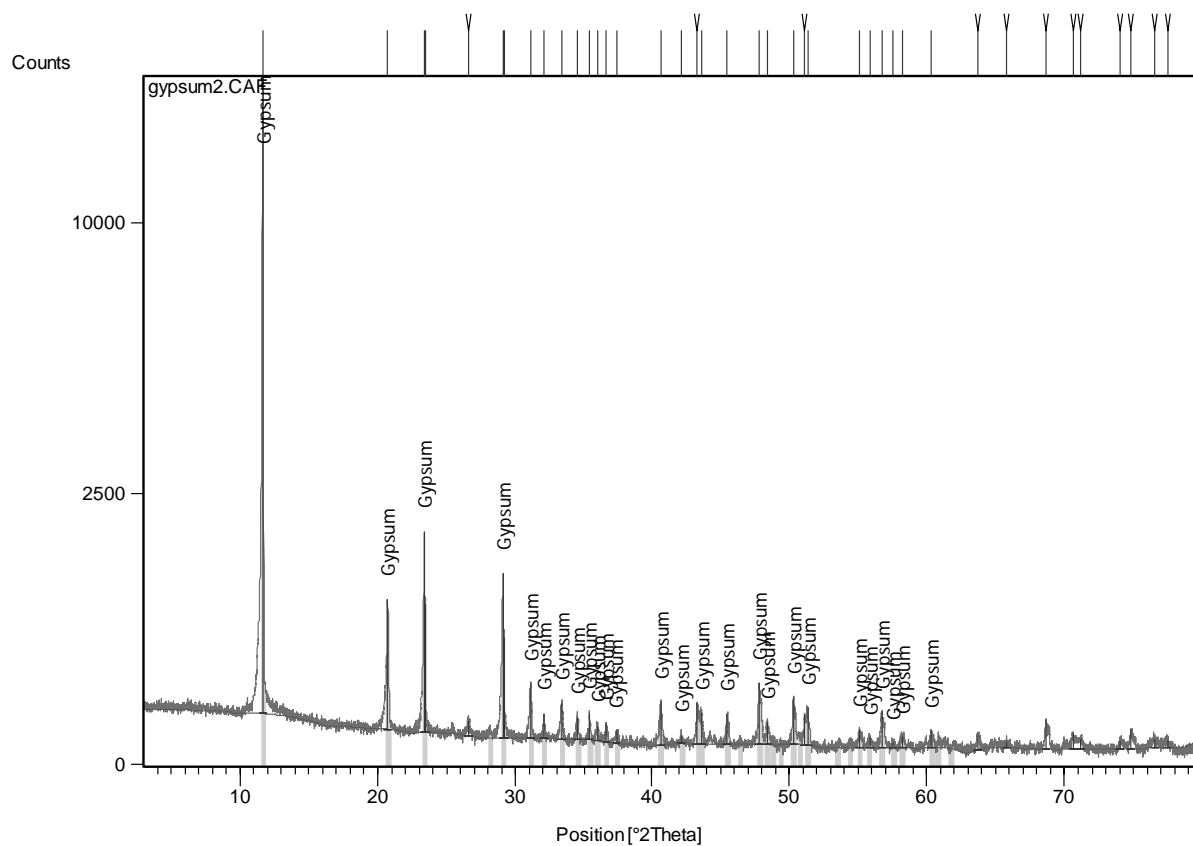


Figure (7): XRD graph of the wet gypsum.

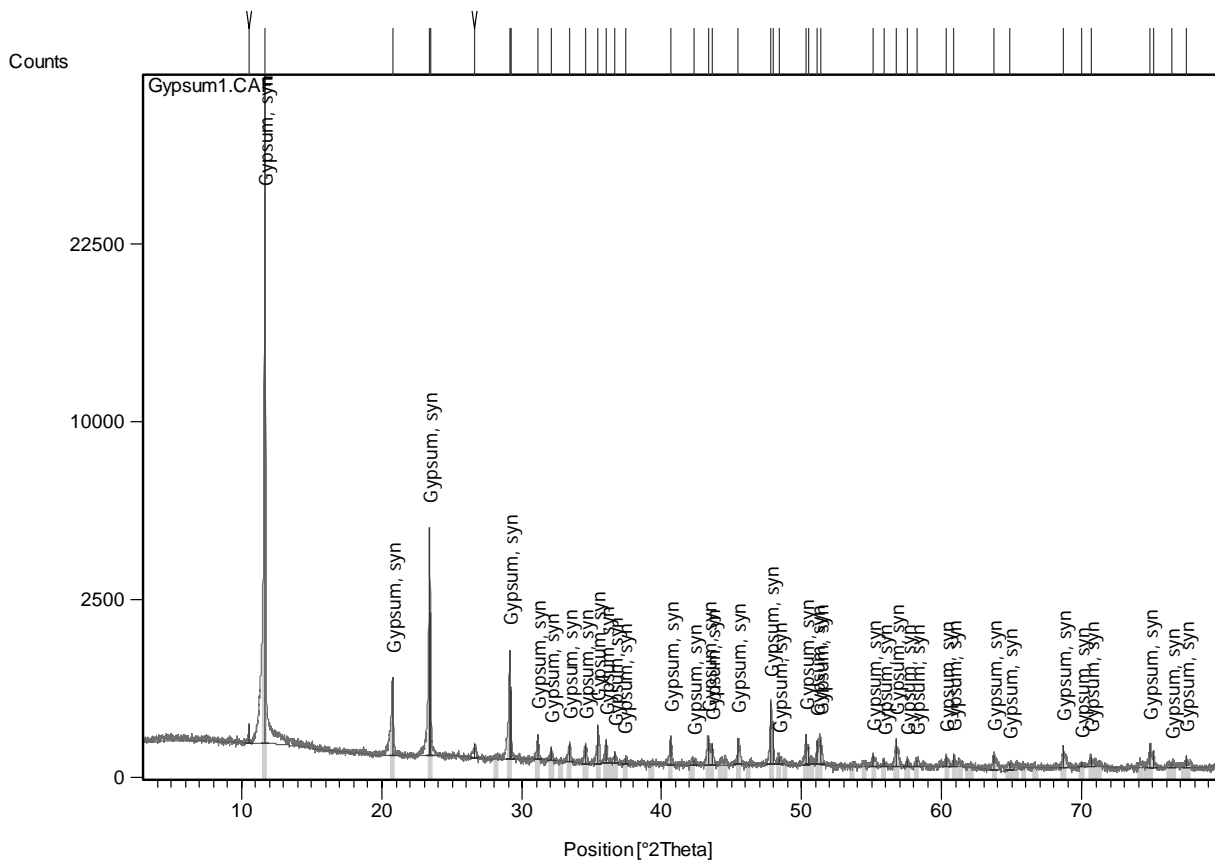


Figure (8): XRD graph of the dry gypsum.

Gravity method revealed two basins in the Aqaba region, one underlying the city itself and the other underlying the investigation area (NRA, 2002).

A vertical section was taken from a wadi in the area located in the southern part of the disposal site, and is described below (Al-Farajat, 2002):

- 0-25m.....Coarse grained reddish to yellowish sandstone inter-bedded with gravel;
- 25-27m...Very fine grained, yellowish, sandy silt;
- 27-34m...Reddish, ferrogenous, coarse to medium grained, unconsolidated sandstone;
- 34-36m...Very fine grained, reddish and yellowish sandy silt;
- 36-42m...Reddish, coarse to medium grained unconsolidated sandstone;
- 42-44m...Flat-lying younger terrace material of fine to

coarse grained sand with some gravel.

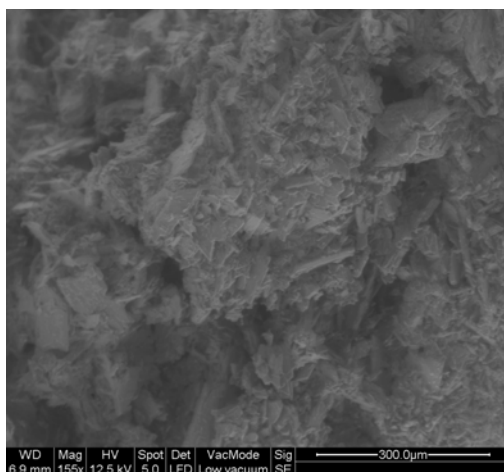
The artificial hills of gypsum extend in width to about 1000 meters (NW-SE), while the length is about 1500 meters (NE-SW). At the end of manufacturing processes in the factory, the solid wastes of gypsum are transported to the disposal site using long moving conveyor belts. The grey colour in the space photo in the northern parts (Fig. 4) is older than those appearing in a lighter white colour in its southern parts.

During the field survey, a 40 m² water pool caused by the leakage of gypsum water between two gypsum hills was found (Fig. 5). The water has a green colour and contains algae all over the water body.

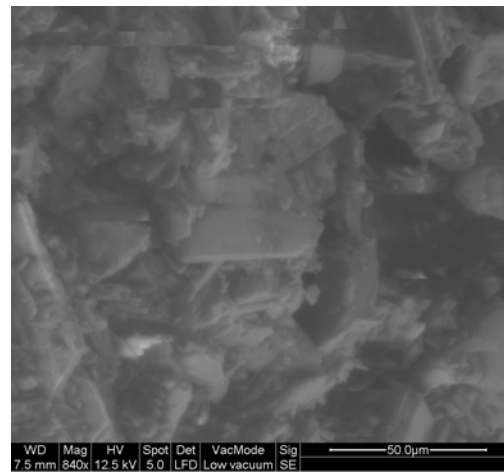
The gypsum deposits are laid along wadis which used to discharge to the gulf water. Two major wadis bound the deposits from both the north and south parts. Some of

these wadis appear in the south eastern part on the space

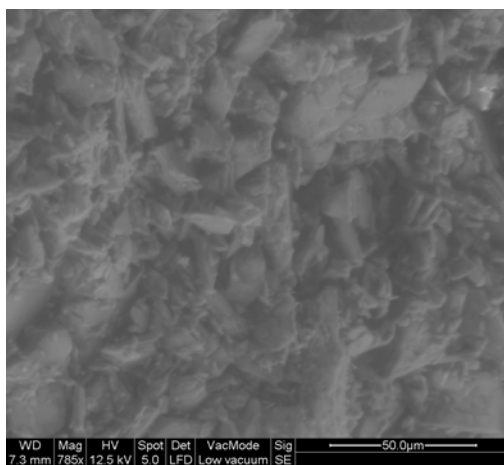
photo in Figure (6).



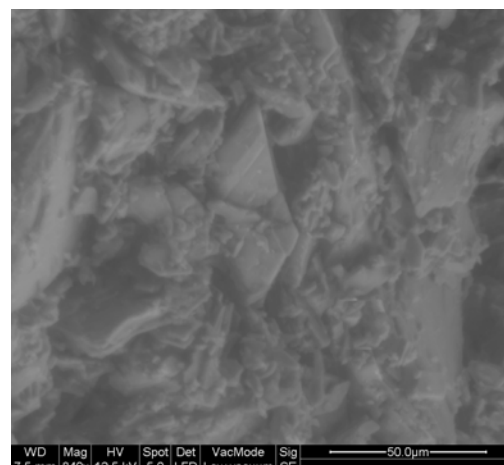
a



b



c



d

Figure (9 a, b, c, d): Images obtained from SEM for gypsum samples. Black colours indicate pores.

Data Acquisition and Analysis

X-ray diffraction method was used to reveal the mineral phases that may form impurities or secondary minerals in the gypsum deposits. This is important concerning the entrapped water in the gypsum and its thermodynamics, i.e. saturation indices of minerals to allow better understanding of the rock-water interactions and the role of the mineralogy of the gypsum deposits in

the development of the water chemistry. The disposal site has been sampled in several locations and at several depths for this purpose, where two results are shown in Figures (7 and 8). Also fresh samples of new deposits have been collected and measured to study any changes in mineralogy that can be attributed to drying process by normal temperature of the area.

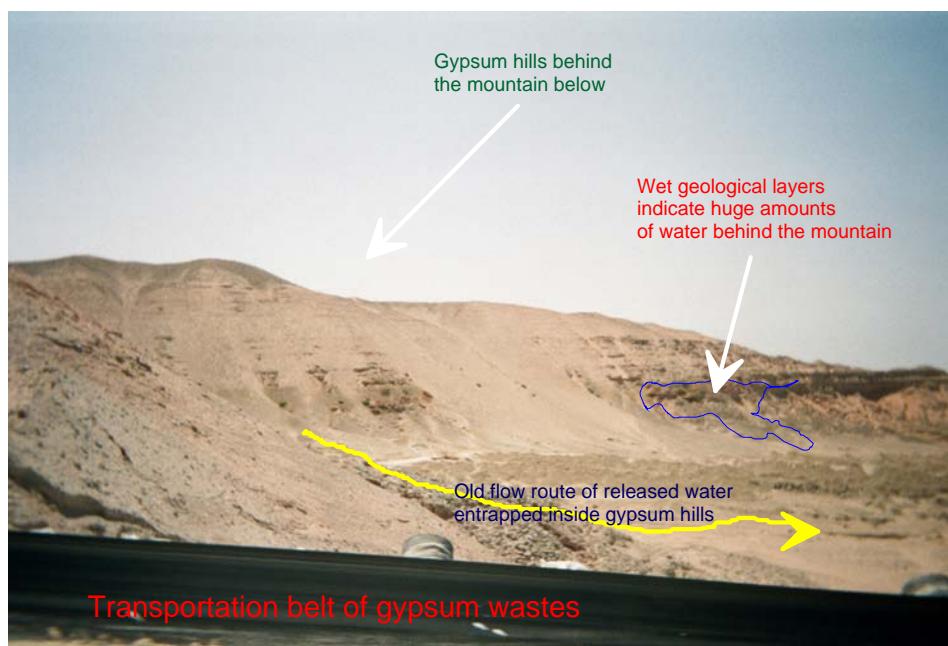


Figure (10): Abnormal growth of plants on the foothills of the mountain indicates leakage of water from the deposits.

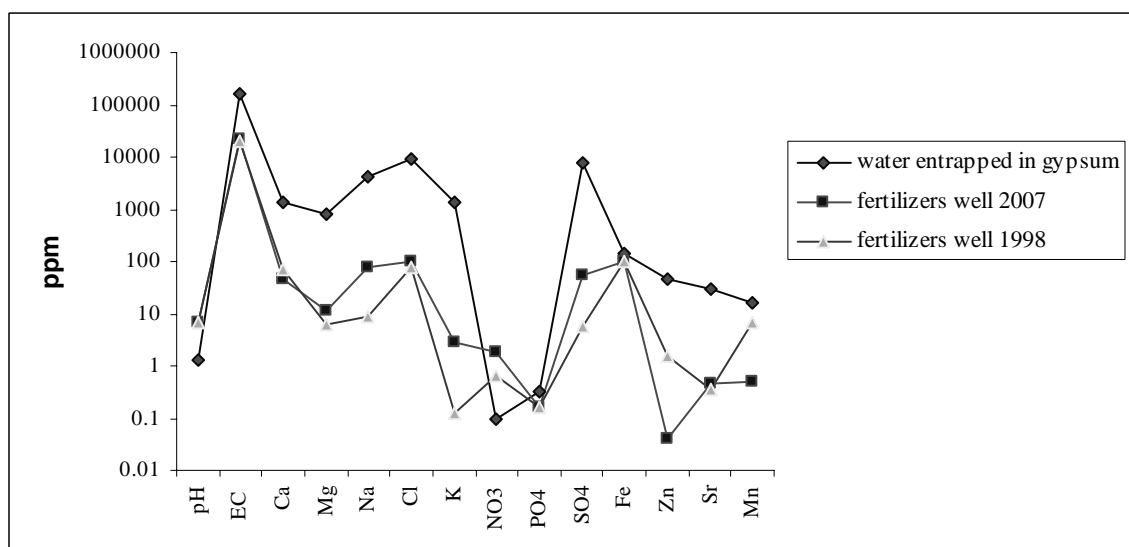


Figure (11): Correlation between chemistry of gypsum water and groundwater.

To shed more light on the geochemistry of the gypsum deposits, 20 samples of fresh wet and dry gypsum from the deposits were taken from selected places of the deposits and exposed to XRF analysis.

Table (1) illustrates the average results of analyses as percentage concentrations of the elements.

With magnifications ranging between 150 and 850 times, the previous gypsum samples were investigated

under the SEM (Scanning Electronic Microscope) to define their textures and the way crystals are stuck to

each other, Figures (9 a, b, c, d).

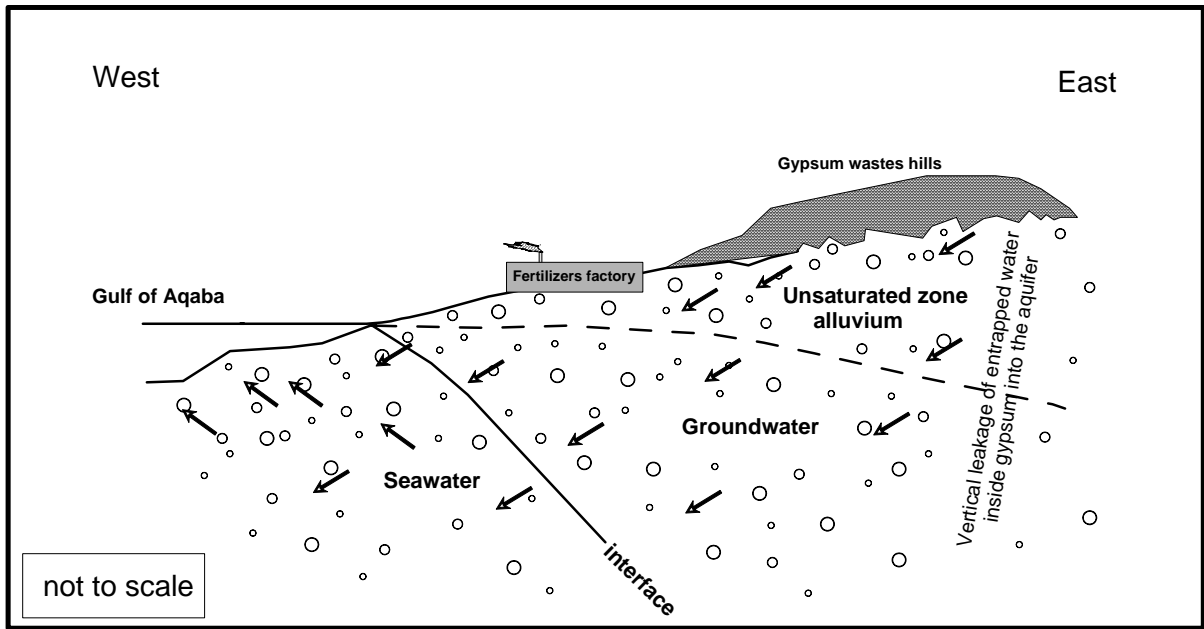


Figure (12): Sketch representing submarine groundwater flow into the Gulf's water carrying pollutants from the gypsum deposits.

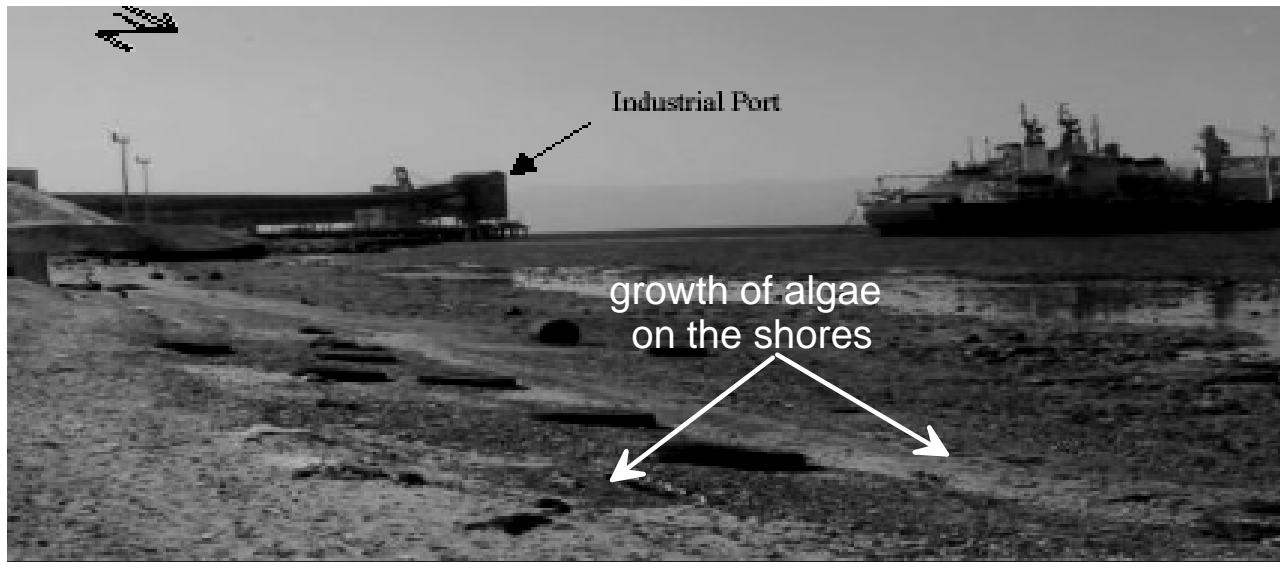


Figure (13): Industrial port of the industrial complex showing growth of algae on the shores (After Al-Ouran, 2005), modified by (Al-Farajat, 2007).

Table (1): Averages concentrations of the elements in the dry and wet gypsum wastes.

Element	dry %	wet %
O	52.418	52.166
F	0.37656	0.79043
Na	0.02636	0.10345
Mg	0.003707	0.003669
Al	0.09613	0.14258
Si	1.3727	1.2722
P	0.33235	0.59649
S	29.359	29.022
K	0.007008	0.007028
Ca	15.916	15.773
Fe	0.014115	0.014315
Rb	0.011208	0.011308
Sr	0.053668	0.0415
Ba	0.013719	0.013014

Geochemical Analysis of the Soil

In the most western part of the gypsum solid waste deposits close to the eastern part of the factory, the alluviums were wet despite the hot summer when the field survey took place. This is an indication on the gypsum water which is entrapped behind the mountain as shown in Figure (10).

For clarification, 3 soil samples from the top, middle and bottom of the wet layers were collected and washed with distilled water for some hours. The extracted water after washing was filtered and then analyzed (Table 2). Several masses of the soil were washed in the same water volumes to allow more detection of low concentrations.

Analysis of Water of Gypsum Hills and Groundwater

One sample from the water released from the deposit was collected (Fig. 5). The water was exposed to chemical analysis on major and trace elements. In addition, one water sample was taken from the groundwater well located in the vicinity of the fertilizers factory, and was also exposed to chemical analysis (Table 3).

In the course of his studies on the southern basin of Aqaba, Al-Farajat (2002) analyzed a water sample from

the fertilizers' well. The results are used in this study to follow historical development of groundwater quality as a result of the growth of gypsum (Figure 11).

DISCUSSION

Considering the measured density of the gypsum samples of around 1.4 gm/cm^3 (bulk density with the internal pores) and the area occupied by the wastes of around 1 km^2 and a thickness of around 14 meters, the total weight of gypsum wastes is calculated to be about 25 million tons. Pores found in the industrial gypsum are responsible for this lowering density. The water content of the fresh gypsum samples was found to be around 20% by weight using drying method. Some of the water is bounded with the chemical formula of the gypsum and the rest is free. Accordingly, around 6 million cubic meters of water are found at the bottom of the hills. This can be true if the systems were closed, but taking evaporation processes and water percolation into consideration, then the amounts of water will not exceed 2-3 millions cubic meters.

The peaks in the graphs of the wet and dry samples (Figs. 7 and 8) reveal that the deposits are consisting only of gypsum and no other mineral phases take place within these deposits. Accordingly, all impurities are not crystalline or chemically related and can be easily diffused with any circulating water. As indicated before, phosphate rocks are the raw industrial material used in producing the fertilizers. Two facts are related to that; the high concentrations of phosphorus which will affect the quality of the entrapped water which may enhance the growth of algae in the surface water, and second the possibility of the presence of radioactivity accompanying products and industrial wastes. Studies carried out by the NRA (2007) indicated that Jordanian phosphate rocks contain around 200 ppm of Uranium.

The phosphorus concentration revealed in gypsum (Table 1) using XRF reached high values in contrary to other elements. This emphasizes that any water circulation in the gypsum wastes will dissolve high concentrations of phosphorus. Accompanying elements to

Uranium like Rubidium and Strontium were found in the gypsum with noticeable concentrations. This issue of

radioactivity is beyond the scope of this study and requires a detailed study.

Table (2): Average results of the analyses of soil water in the alluvial deposits.

ANALYSIS	UNIT	5GRAM OF SOIL	20GRAM OF SOIL	30GRAM OF SOIL	50GRAM OF SOIL
pH		7.01	7.02	6.73	7.00
Conductivity	μ S./cm	2003	6560	9300	14280
Ca Hardness as CaCO_3	ppm	880	3260	4850	7720
Chloride	ppm	527	2100	3200	5400
SO_4	ppm	180	530	710	1010
T.D.S.	ppm	1302	4264	6045	9282

Table (3): Chemical analyses of gypsum water and groundwater.

Element (ppm)	Water entrapped in gypsum	Fertilizers' well 2007	Fertilizers' well 1998 (Al-Farajat, 2002)
pH	1.5	6.9	6.88
EC μ S./cm	162100	21123	19650
Ca ppm	1300	44.5	68.54
Mg ppm	800	11.24	6.02
Na ppm	4162.5	78.875	8.66
Cl ppm	9217	96.8	80
K ppm	1400	2.7401	0.12
NO₃ ppm	0.1	1.811	0.656
PO₄ ppm	0.321	0.167	0.158
SO₄ ppm	7644	54.1	5.61
Fe ppm	135.8	100	95.85
Zn ppm	47.21	0.04	1.5
Sr ppm	29.34	0.463	0.36
Mn ppm	16.56	0.506	6.53

Figures (9 a, b, c and d) resulting from SEM investigations show elongated gypsum crystals with no specific trend of direction. Also, it is well shown in the figures that the crystals are surrounded by many micro-pores. This improves and enhances the ability of water entrapped inside gypsum hills to better circulate, especially because the pores seem to be connected to each other resulting in good permeability. Worth mentioning here is that deep elongated cracks and joints are present all over the deposits which enhances water flow and circulation.

The entrapped water in some places in the hills leaks laterally and is then retarded by low permeability zones of alluviums. This led to the growth of some plants as shown in the area surrounded by black lines in Figure (10). When water flows to weak zones such as fractures, it flows at the surface.

The analyses (Table 2) of the soil impacted by lateral leakage of gypsum water show that the alluvium layers are affected by gypsum water. It seems that the samples are of high TDS values, and they contain high amounts of SO_4 indicating the origin of the water and its circulation

The process will go on until the available phosphate or nitrate is used up. The reverse of this reaction takes place to enable the decay of algae (Drever, 1997).

Lloyd and Heathcote (1985) mentioned that the average seawater consumption includes the concentration of NO_3^- and HPO_4^{2-} of 0.5 and 0.07 mg/l, respectively. These two nutrients are considered the limiting factor for eutrophication. Under these conditions, the algae in the marine environments grow and decompose in a balanced cycle, forming no negative impacts on this environment.

Total phosphorous levels higher than 0.03 mg/L contribute to increased plant growth, while total phosphorous levels above 0.1 mg/L may stimulate plant growth sufficiently to surpass natural eutrophication rates (Electronic reference 2).

In eutrophication processes, microscopic floating plants, known as algae, multiply rapidly when fertilized by phosphorus. These algae cloud the water making it difficult for larger Submerged Aquatic Vegetation (SAV) to get enough light. The SAV may dieback reducing available habitat of aquatic animals. When the algae themselves eventually die, they decompose. During decomposition, dissolved oxygen is removed from the water. Lowered oxygen levels make it difficult for other aquatic organisms to survive (Electronic reference 3).

Looking at the part of the reactants from the previous equation, the requirements for the reaction to go forward to produce algae in the coastal water of the Gulf of Aqaba at the contact with the industrial complex are available. In the groundwater of the aquifer below the factory, the concentrations of PO_4 were found more than that documented and reached 0.03 mg/L (see Table 4). Figure (13) is a photo which was taken for the industrial port to the west of the factory and represents growth of algae in the shores bordering the industrial complex.

In a study carried out for the Aqaba Region Authority in 1993 ("Aqaba Coastal Resources Environmental Management Study in Jordan"), the phenomenon of eutrophication was attributed to the phosphate dust particles deposition in the sea water (from porting processes).

In a long term record study (14 months) for the

Marine Science Station in Aqaba in 1998, the environmental quality of the Gulf of Aqaba in the coastal areas at four locations and one meter depth was defined. Natural and anthropomorphic factors resulted in positively modifying the chlorophyll concentration. Values of NO_3 and PO_4 were also positively modified and found sometimes to exceed 0.5 mg/l and 40 $\mu\text{g/l}$, respectively. Al-Ouran (2005) registered higher values in the seawater, emphasizing the increase of pollution.

The previous measured concentrations are approaching the specified threshold values to start eutrophication (see equation 1). Lau (2002), Smith (1998), Sewell (1982) and Johnes (1996) mentioned similar values of P and N in water released to surface water bodies to start eutrophication.

The characteristics of eutrophication processes in reservoirs and lakes are quite specific in the semi-arid areas. Not only do the problems derived from eutrophication affect the quality of water, but they also have an adverse effect on the fauna. Along with the porting processes of the products of fertilizers and the possible transportation of gypsum dust particles with air into the marine water, comes the submarine discharge of the polluted groundwater with the gypsum water to initiate the phenomenon of eutrophication in the shores of the industrial port.

SUMMARY AND CONCLUSIONS

In this article, the impact of the solid industrial wastes disposal site of gypsum on the groundwater has been studied. Industrial wastes of gypsum have been found not only to cause visual pollution in the surrounding as it was known by the environmental authorities in the governorate, but also to impact groundwater quality, and consequently the marine water and life of the Gulf of Aqaba in contact with the industrial complex. Eutrophication is one type of impact which was related in this study to the submarine groundwater discharge of water enriched with P and N coming from the percolated free water of gypsum. The concentrations of the former elements exceeded the known concentrations that can start growth of plants in water bodies.

Flux of groundwater into the marine water body is still taking place around the year and accordingly the eutrophication process is still taking place and may be increased more and more, unless scientific solutions are applied to alleviate any negative impacts.

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- Acknowledgment**
- The author acknowledges the project of FFF in Jordan (University of Jordan – Faculty of Engineering, 2007) to support the study, and the Jordanian Phosphate Company and Industrial complex to smooth the field survey of this work.
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IMPACTS/WATERPOLLUTION/WATER_HOME:HT
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Electronic reference 2: <http://www.leo.lehigh.edu/envirosce/watershed/wq/wqbackground/phosphatesbg.html>

Electronic reference 3: <http://www.agnr.umd.edu/users/agron/nutrient/Factshee/Phosphorus/Eutrop.html>